

PATENT SPECIFICATION

(11) 1 396 072

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(21) Application No. 25665/73 (22) Filed 30 May 1973
 (31) Convention Application No. 56444/72 (32) Filed 8 June 1972 in (19)
 (33) Japan (JA)
 (44) Complete Specification published 29 May 1975
 (51) INT CL: D02J 3/18; D06M 11/18
 (52) Index at acceptance

D1W 6 7A
 C1A D46 G11 G11D46 G13 G13D46 G24 G24D46 G39
 G39D46 G3 G3D46 G4 G4D46 N11 N13A N24A
 N39AX N3 N4AX NX1D
 D1F X
 D1P AX B5A B5B B5C C1G C1H3A C1H3B C1H3X C1J
 C1L1 C1LX

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(54) CONDUCTIVE SYNTHETIC FIBERS

(71) We, ASAHI KASEI KOGYO KABUSHIKI KAISHA, of No. 25-1 Dojimahamadori, 1-chome, Kitaku, Osaka, Japan. A body corporate of Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to synthetic organic polymer fibers having electric conductivity (hereinafter referred to simply as conductivity) and a method for producing same. More particularly, this invention relates to synthetic organic polymer fibers having an electric resistivity of 10^9 ohm/cm or less whose surface is covered by a firmly adherent layer of a metal compound. Such fibers are useful for eliminating static electricity of fibrous products by incorporating with other synthetic fibers and can be used in applications which conventional synthetic fibres could not previously have entered e.g. as substitutes for expensive metal fibers.

General purpose synthetic organic fibers such as polyamide fibers, polyester fibers, acrylic polymer fibers and polypropylene fibers have an electric resistivity greater than 10^{10} ohm/cm and hardly allow any current to flow therethrough. The harmful effect of static electricity in synthetic fiber products is due to this property.

There are various methods for eliminating the harmful effect of static electricity, but a method which relies on the blending of conductive fibers (fibers having a good electric conductivity) into synthetic fiber products is not only applicable easily in the initial stages of manufacture of fibrous products starting from loose fibers but also satisfactory in the practical antistatic effect and their durability. In the blending of conductive fibers, metal

fibers are ideal raw materials considering conductivity and their durability. However, since metal fibers are not suitable for mass production, they are not commercially advantageous raw materials. Further they are inferior in mechanical properties and properties necessary for processing at the time of blending into fibrous products.

It is also known that antistatic products which are not inferior to metal fibers-containing products can be obtained by incorporating, in place of metal fibers, fibers whose conductivity is improved by introducing conductive substances inside or on the surface of general purpose synthetic organic polymer fibers, into fibrous products, e.g. carpets and sewing machine thread.

To manufacture such conductive synthetic fibers, there has been employed a method in which a layer of a metal is formed on the surface of fibers by a chemical plating method, an electro-plating method or a metallizing method. However, the chemical plating method can produce improved fibers having a large conductivity but poor durability, and requires complicated pretreatment steps such as surface corrosion, sensitization, and activation, resulting in a high product cost. The electro-plating method is liable to bring about unevenness of deposit of metal due to uneven current density and is accompanied with technical difficulty in applying to fibers. The metallizing method has the drawback that the metal coating is liable to be peeled off on account of poor adhesive strength.

At any rate, these physical or chemical methods are not adequate as methods for modifying general purpose synthetic fibers into conductive fibers, cheaply in a commercial process.

Further, there is a method in which fine powders of conductive substance are incorpo-

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ated into a synthetic organic polymer and the resulting blend is subjected to spinning. However, in order to obtain a value of electric resistivity in the order of 10^6 ohm/cm by this blending and spinning method, it is necessary to incorporate more than 50% by weight of powdered conductive substance such as metal powder, (see B. E. Gynt, Research and Application of Conductive Polymers, translated into Japanese by Tadotoshi Sadamasa, published by Yokokawa Shoin). Thus, the method is not an adequate one for shaping fine practical fibers.

Also, there is known a method in which metal powder as conductive fine powder is attached by melting onto the surface of thermoplastic polymer fibers, or a method in which metal powder is blended with a thermosetting resin and fibers are coated with the resulting blend, but it is impossible to obtain fibers having an electric resistivity of 10^6 ohm/cm or less unless secondary processing properties, and handle (flexibility and softness) are sacrificed. In other words, according to the metal adhesion method, if metal is made to adhere in an amount of more than 50% by weight based on the weight of fibers, a resistivity of 10^6 ohm/cm or less can be obtained, but the thickness of the coated film becomes greater, and in the case of multifilament yarns, there is a drawback of cohesion of monofilaments into a cord-like form.

According to the present invention, there is provided a conductive synthetic fiber having an electric resistivity of 10^6 ohm/cm or less comprising a layer of a metal compound on the surface of a thermoplastic synthetic polymer fiber, said metal compound being obtained by subjecting metal powder attached to the surface of said thermoplastic synthetic polymer fiber to an oxidation treatment as herein defined, the metal compound being insoluble in water and dry cleaning solvents.

In this Specification, we use the terms "oxidation" and "oxidising" in their widest sense as any treatment which increases the oxidation number of the metal from zero to a positive value. Thus the oxidation treatment suitable for use in the present invention includes not only oxide formation, but also for example sulfurization, chlorination and carbonation.

We have found that synthetic organic polymer fibers whose surface is coated with metal powder show unexpectedly a low conductivity, but when these fibers are treated in an oxidising atmosphere, the conductivity is increased. Surprising enough, it is possible according to this method to obtain fibers having as low an electric resistivity as 10^2 to 10^5 ohm/cm which is comparable to that of the fibers having a continuous metal layer, obtained according to chemical plating method.

Thus, the present invention lies in conductive synthetic fibers (1) having a layer of a metal compound undetachably supported on the surface of synthetic organic thermoplastic polymer fibers having substantially no conductivity, and (2) showing an electric resistivity of 10^6 ohm/cm or less. (Said synthetic organic thermoplastic polymer fibers will be hereinafter referred to simply as thermoplastic synthetic fibers.) The metal compound layer on the surface of such fibers, is not detached easily by abrasion or washing. It is a feature of the present invention that the above-mentioned undetachability is caused by the strongly bonded state of the compound on the surface of the fibers, but not by using a high molecular weight substance as a binder.

Thermoplastic synthetic fibers herein referred to are those of melt-spinnable polymers such as polyamides, polyesters and polyolefins. Particularly, polyamide fibers have excellent adhesiveness to metals and metal compounds and hence conductive fibers having superior durability, i.e. superior abrasion-resistance and washing-resistance can be obtained therefrom.

The metal compound used in the present invention is obtained by increasing the oxidation number of a metal from zero to a positive value.

As the oxidizing agent, hydrogen sulfide, oxygen, O_2 -containing gas such as air, halogen, hydrogen peroxide, a mixture of carbon dioxide, water and air or oxygen, can be illustrated. The oxidation is liable to occur in the presence of water. Further, the resulting metal compound must not be soluble in water or dry-cleaning solvents.

Preferable metal compounds used in the present invention include sulfides, oxides and carboxnates of copper, zinc, lead, silver, aluminum, iron and the alloys of the foregoing metals. Compounds which yield more preferable results are sulfides and oxides. These sulfides and oxides are also preferable in view of the simplicity of treatment and the performance of the products.

It is a characteristic point of the present invention that the metal compounds form a coating layer even without any adhesive.

The coating state of the metal compounds in the conductive fibers of the present invention, when observed through an electron microscope, is considerably different in the appearance of powder itself and the fineness of coating, from the coating state of metal powder. See Figs. 2 and 3 of the accompanying drawings.

In spite of the generally accepted fact that metal compounds are all poorer in conductivity than the simple substances of metals, metal compound-carrying fibers show as low an electric resistance as comparable to those of chemically plated fibers. This is really a surprising fact.

For example, the electric resistivity of fibers on the surface of which copper powder is uniformly attached is $10^{10} \Omega/cm$ at the highest, but electric resistivity of fibers after the cop-

per powder is converted into a sulfide with hydrogen sulfide becomes $10-10^3 \Omega/cm$, that is, the conductivity is remarkably increased.

The reason of this strange phenomenon is 5 not clear, but it is presumed that since the metal is in an oxidized state, it is electrically charged, and as the result, molecules of for example water and carbon dioxide in the air possessing polarity, are secondarily coordinated 10 with the particles of the metal therebetween to promote the flow of current.

The amount of the metal compound made 15 to adhere is $10^{-3} g/m$ or more as converted into the weight of the metal, per filament of common range of denier. In this case, an electric resistivity of $10^5 \Omega/cm$ or less can be obtained. When the amount as converted into the weight of the metal, is in the neighbourhood of $10^{-10} g/m$, the coated layer becomes 20 discontinuous showing elevated electric resistance. Electric resistivities of $10^5 \Omega/cm$ or less can be obtained in the case where the surfaces of fibers are coated with a substantially continuous layer of the metal compound. The 25 thickness of such a layer is in the range of $0.1 \mu-20 \mu$.

The fibers having the metal compound made 30 to adhere thereonto can be in the form of monofilament, multifilament, cord, in some instance, tow or staple fiber. The denier of monofilament of the above-mentioned form of fibers is commonly in the range of $2-20,000$ denier. It goes without saying that it can be selected according to the application field 35 where the conductive fibers are used. Accordingly, the denier should not be construed as limitative. In the present invention, an embodiment of conductive fibers of sheath and core type composite structure in which the 40 metal compound is supported on the surface of the sheath of polyamide polymers, is a most advantageous one. The polyamide polymers firmly support the metal compound on their surface whereby resistance against detachment 45 is increased and permanent conductivity is ensured. Core components can be selected from any melt-spinnable polymers such as polyamides, polyesters and polyolefins.

The conductive synthetic fibers of the present invention can be obtained by making 50 metal powder uniformly adhere on the surface of thermoplastic synthetic resin fibers, and then oxidizing said metal powder.

The adhesion of metal powder on the surface 55 of the fibers as the first step, can be attained by a process in which filaments or bundles of filaments of thermoplastic synthetic fibers are in advance sprinkled with metal powder and then bringing the surface layer of 60 the fiber section into molten state by heating to make said metal powder adhere thereonto, or another process in which filaments or bundles of filaments are passed through a vessel containing metal powder. Of these two 65 methods, the former is advantageous. It is dif-

ficult in the case of bundles of filaments to bring only the surface parts of each filament into molten state and maintain this state further in the incorporating step of metal powder. In such a case, there is a fear of impairing 70 mechanical properties of fibers.

There is a difference in the degree of adhesion of the metal powder depending upon the kinds of polymers constituting the fibers. The use of fibers having a sheath and core cross-sectional structure is most advantageous in 75 industrial operation. Namely, fibers are prepared through composite spinning by using as the sheath component, a polymer having a lower melting point, then attaching metal powder onto said fibers and making the metal powder adhere onto the fibers at the time of the attachment or by subsequent heating at a temperature higher than the melting point of the sheath polymer.

From the view point of adhesive property and melting point, polyamide polymers are 80 preferable for a sheath polymer. For example, two component or three component copolyamides such as (nylon 6/nylon 66/nylon 610), (nylon 6/nylon 66/nylon 12), (nylon 6/nylon 612), modified polyamides such as N-alkoxy-methyl-nylon 6, N-alkoxymethyl-nylon 66, 85 can be illustrated as such polyamide polymers, but, from the technical standpoint of spinning of composite fibers and adhesive property of metal powder thereto, melt-spinnable copolyamides are most suitable. The kind of thermoplastic high molecular weight substances useful as a core component of the composite fibers, may be varied depending upon the combination thereof with the sheath component, particularly due to the relationship of the melting point of the latter, but in general nylon 6, nylon 66, copolymer of nylon 6 and nylon 90 66, nylon 610, nylon 612, and polyethylene terephthalate, are suitable.

The spinning of sheath and core type composite fibers whose sheath part is a polyamide having heat-melting and adhesive property, is 95 carried out by using a known composite fiber spinning apparatus.

The volume ratio of sheath/core, is selected 100 from the range of $1/5$ to $5/1$, and $1/5-3/1$ is suitable. Volume ratios less than $1/5$ and greater than $5/1$ are not good in order to maintain the fiber state and mechanical properties even under the heat during the step of heat adhesion of metal powder and to avoid the mechanical detachment and falling-off of 105 attached metal powder.

Metal powder is preferably of simple substances or alloys of copper, zinc, lead, silver, aluminum or iron. When the average particle diameter of the powder is 5μ or less, the 115 smaller the particle size, the more uniform and continuous the adhesion onto the surface of the fibers and also the more stabilized the conductivity of the fibers obtained after the subsequent processing step of oxidation. When 120 125 130

the particle size of the metal is greater than 10 μ , uniform coating by the adhesion onto the surface of the fibers becomes difficult, abrasion resistance of the metal compound layer after the oxidation processing is reduced and effect for reducing electric resistance is lowered. 5

Both scale form and spherical form of metal powder can be used. As for the heat treatment temperature of the fibers having metal powder made to adhere thereonto, unless the temperature is the melting point of polymer of fibers or higher, the powder on the surface of fibers is difficult to adhere firmly onto the fibers. 10

In the case of the above-mentioned sheath-core-type composite fibers, it is preferable to select a temperature for treating fiber surface of above the melting point of the sheath component polymer and below the melting point of the core component polymer. When the heat treatment is carried out at a temperature in this range, only the sheath component polymer melts (only the surface part of fibers is melted), to give better adhesion of metal powder, and at the same time, the tenacity and the elongation of composite fibers are hardly reduced, because the molecular structure as fiber, of the thermoplastic high molecular weight polymer in the core part, is not disturbed at all. 15

On the other hand, when the heat treatment is carried out at a temperature lower than the melting point of the sheath component polymer, the melting of fiber surface does not take place, and hence metal powder is not supported adherently on the fiber surface and liable to be detached easily by washing and abrasion. When the heat treatment is carried out at a temperature higher than the melting point of the core component polymer, the thermoplastic high molecular weight polymer in the core part undergoes influence of heat and the molecular structure of fibers is disturbed exceedingly. As a result, break of filaments occurs frequently during the time of heat-adhesion. 20

The amount of metal powder made to adhere must be such an extent that the surface of fibers is coated uniformly by the metal powder. According to our research, a satisfactory result can be obtained if 10 $^{-10}$ g or more, preferably 10 $^{-9}$ g or more per meter of monofilament is made to adhere. In other words, if such an extent of adhesion is carried out, fibers having an electric resistivity of 10 8 Ω/cm or less can be obtained showing stabilized result. An adhesion amount of less than 10 $^{-10}$ g does not give a continuous coating layer on fibers, and also the conductivity is not so good. If the above-mentioned amount is carried by fibers, the thickness of the metal powder layer will be in the range of 0.1 μ —20 μ according to the observation of photographs obtained using an electron microscope. 25

There are various embodiments for the steps of attaching metal powder and making them adhere onto fibers. It is a most desirous step to draw out yarns (raw material yarns for fabrics) having been melt-spun from a spinneret and stretched, from a bobbin, lead them into a vessel containing metal powder and pass the resulting yarns through a heating zone. It is not a preferable process from the view point of the handling of metal powder and physical properties of yarn to make the metal powders adhere onto the fibers having been extruded but not solidified yet in the melt-spinning. 30

It is also not preferable from the view point of uniform adhesion and not advantageous in the commercial production to make metal powders adhere onto unstretched yarns. 35

As for the process for attaching metal powder onto fibers, by passing filaments through a vessel containing metal powder, there can be illustrated a process in which filaments are passed through a metal powder layer floating upon a water bath and a process in which filaments are passed through a vessel containing floating heated metal powder to effect simultaneous attachment and heat-adhesion of the metal powder. 40

One example of such a process will be described with reference to the accompanying drawings. 45

Figure 1 is a schematic diagram showing a process for making metal powder adhere onto the surface of fibers useful in the process of the present invention. 50

Figure 2 is an electron microscopic photograph of the fibers having brass powder made to adhere thereto (taken by a scanning type electron microscope). 55

Figure 3 is also an electron microscopic photograph of the fibers having brass powder made to adhere thereto and then sulfurized (taken by the same microscope). 60

In Figure 1, numeral 1 shows a bobbin of raw material filaments, numeral 2 shows unwound filaments, numeral 3 shows a humidifying part, numeral 4 shows metal powder, numeral 5 shows a vessel containing metal powder, numeral 6 shows a heat-treatment cylinder, numeral 7 shows wound-up filaments, numeral 8 shows feed rolls, numeral 9 shows delivery rolls and 10 shows a vibrating apparatus. The filaments 2 unwound through a guide are humidified in the humidifying part 3 and passed through a metal powder vessel 5 filled with metal powder 4 to attach the metal powder onto the surface of the filaments running through the vessel. 65

Successively the filaments are allowed to run through the inside of the heat-treatment cylinder 6 maintained at a predetermined temperature to melt the surface of fibers and simultaneously to make the metal powder adhere onto the surface of the fibers by heat-melting, and the resulting filaments are taken up as wound-up filaments 7. 70

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The above-mentioned process can be applied either to unstretched yarns or stretched yarns depending upon whether a tension is applied to the composite filaments running through the heat-treatment cylinder. 40

5 Thus obtained yarns having metal powder made to adhere thereto has an electric resistivity of at most $10^{10} \Omega/\text{cm}$ when viewed only from the standpoint of conductivity. It can- 45

10 not be helped to say that performance as conductive fibers is still low. By subjecting the metal powder made to adhere to the surface of fibers by heat, to subsequent oxidation treatment, conductive fibers can be obtained. 50

15 The oxidation treatment of metal powder referred to herein is the treatment carried out to increase the oxidation number of metal powder from zero to a positive value. 55

20 For example, it means to subject a metal powder to oxidation treatment to convert into its oxide, sulfide, or carbonate. 60

25 The method for treating the fibers processed with metal is very simple. Only an application of a known chemical reaction thereto will be sufficient. The step should be selected depending upon the kind of oxidation treatment and chemical reactivity. 65

30 For example, in case of sulfurization treatment of fibers having copper powder made to adhere thereto, since the rate of the sulfurization treatment is extremely rapid, the desired treatment can be attained simply by contacting the fibers having the metal powder made to adhere thereto, with humid hydrogen sulfide 70

35 gas, successively to the attachment treatment of the metal powder. 75

In the case of oxide formation, the object can be attained by allowing fibers having metal powder adhere thereto to stand in the atmos-

phere of oxygen gas at a high temperature under a humid condition for 2 to 7 days. In this case, since the oxidation treatment rate is slow, it is preferable to wind up on a skein and subject to the treatment in a batch manner. 40

In general as for the conductivity of metals, a good conductivity is shown when metal-metal bonds exist i.e. at zero oxidation number. In the case of compounds of metals, i.e. at a positive oxidation number, the conductivity effect is exceedingly reduced. But surprisingly, and contrary to generally accepted conventional ideas, the fibers obtained by the processing with metal according to the present invention have, after the oxidation treatment, an exceedingly increased conductivity, i.e. as low an electric resistivity as $10^5 \Omega/\text{cm}$ or less. 55

The conductive fibers obtained according to the present invention have the possibility of usefulness in wide varieties of application by making the most of superior electric conductivity. 60

For example, it is possible to solve the problem of basic troubles of synthetic fibers due to the static electricity in the atmosphere of low humidity which troubles have been the greatest drawback for synthetic fibers, merely by blending thereinto a small amount of the conductive fibers of the present invention. 65

As examples of special utility, fabrics made of the fibers of the present invention can be used for protective clothes for workers under a high voltage power transmission and a high electromagnetic field, and shielding fabrics for protecting against harmful electromagnetic effect at the time of precise measurement, by utilizing the very efficient shielding effect of microwaves as shown in Table 1. 70

TABLE 1

Fabrics comprising the conductive fibers of the present invention	Percentage transmission of microwave	Percentage reflection of microwave
Fibers coated with copper sulfide	0.2%	99.8%

Conditions of measurement: a microwave having a frequency of 9 GigaHertz is sent from a location at a distance of 20 m from a receiver enclosed in a fabric. Percentage transmission was measured from the intensity of oscillation of the received microwave. 95

80 Further it is possible to use the products of the present invention as raw materials for curtains and snow-melting-tent having a heating mechanism by utilizing such a low electric resistivity as $10^3 \Omega/\text{cm}$. 100

85 As above-mentioned, conductive fibers useful in wide varieties of application field can be provided economically only by a combination of extremely simple steps. 105

Following Examples are given to illustrate further the present invention. 95

Example 1.

Dried chips of nylon 6 (relative viscosity as measured in 98% sulfuric acid at 25°C: 2.42, m.p.: 218°C) and copolyamide of nylon 6/nylon 612 (mol ratio of 65/35; relative viscosity as measured in 98% sulfuric acid at 25°C: 2.52; m.p.: 148°C) were separately melted at 280°C and 240°C, respectively, and subjected to composite spinning using a sheath and core type composite spinning machine to prepare composite filament yarns of concentric sheath and core type consisting of a core of

5 nylon 6 and a sheath of the copolyamide with a sheath to core ratio of 2:1 by weight which were stretched to 3.5 times the original length according to a conventional method to give composite filament yarns of 70 d/9 f (d/f = denier/filaments).

10 Then brass powder having an average diameter of 2μ and a composition of Cu/Zn of 70/30 by weight was made to adhere by heating, to the surface of the resulting composite filaments through the processing step of Fig. 1. Namely, composite yarns 2 were allowed to run through the inside of a powder container 5 provided with a vibration apparatus 10 and containing brass powder 4 composed of 70 parts by weight of copper and 30 parts by weight of zinc (mean particle diameter of 2μ) at a velocity of 50 m/min., successively led to a heating cylinder 6 having an inner diameter of 70 mm and a length of 1500 mm and taken up at a velocity of 60 m/min.

15 By setting temperatures of the inside of the heating cylinder at 130°C, 190°C and 220°C, the melt-adhesion property of brass powder was estimated. As a result, at temperatures of 130°C and 190°C, the yarns were taken up without any troubles, but, at 220°C, yarn breakage very often occurred and take-up was difficult.

20 The resulting yarns having the metal powder made to adhere thereonto (which will be hereinafter abbreviated as metal powder-carrying fibers) were washed for 10 minutes, with stirring, three times with a 5% (by weight) aqueous solution of a neutral detergent with a bath ratio of 1:50 by weight, followed by water-washing five times. Thereafter, the amount of metal powder made to adhere onto the surface of the fibers was measured. The results are shown in Table 2.

25 In the case of the heat-treatment at 130°C, brass powder adhered only from place to place, while when the yarns were heated at 190°C and 220°C, the surface of the yarns was completely coated with brass powder showing splendid yellowish red luster of brass. Further, the tenacities and elongations of the metal powder-carrying yarns obtained in this example were measured and the results are shown also in Table 2. As seen in the table, in the case of heating at 220°C, the tenacity and elongation were both remarkably reduced.

30 This is due to too high a temperature at the time of adhesion by heating which has disturbed the fiber form of core component of nylon 6.

35 Resultant brass powder-carrying yarns were taken up on skeins each in an amount of 50 g. and allowed to stand in the atmosphere of a desiccator having a relative humidity of 100%,

40 a partial pressure of 300 mm Hg of H₂S at room temperature whereby the brass powder on the surface of the fibers was sulfurized showing a characteristic black color of metal sulfide. After sulfurizing treatment for 2 hours in said atmosphere, the sulfurized brass-carrying yarns were washed with water twice and dried at 105°C for 5 hours. After drying, the electric resistances of said metal-carrying yarns were measured in a thermostat at room temperature (25°C) and a relative humidity of 40% with an electric resistance measurement instrument TR-6S type of Takeda Riken Kabushiki Kaisha. Similar measurement was carried out with regard to the metal powder-carrying yarns before sulfurizing.

45 The result obtained is shown also in Table 2. The metal-carrying fibers having brass powder made to adhere by melting at 190°C and 220°C showed only an electric resistivity in the order of $10^{10} \Omega/\text{cm}$ at the highest value in spite of the fact that the surfaces of the fibers are apparently wholly covered by brass powder (refer to Fig. 2). On the other hand, the brass powder-carrying fibers after the treatment of sulfurizing showed as extremely low a value of electric resistivity as in the order of $10^2 \Omega/\text{cm}$.

50 Figures 2 and 3 are photographs (taken by a scanning type electron-microscope (JSM-U3 type of Nippon Denshi K.K., magnification of 1050) of the surfaces of the metal powder carrying fibers obtained by melt-adhesion of brass powder at 190°C and the same surfaces after sulfurizing treatment.

55 It is evident that there is a notable difference between Figures 2 and 3. In Figure 2, scale-form particles of brass powder are piled up one above another completely covering the whole fiber surface but there are gaps between each particle. However in Figure 3, it is a characteristic feature of this case that sulfurization of brass powder not only changes the surface form of individual particles but also reduces the gap between each particle.

60 It is assumed that such a strange phenomenon as the fact that the metal compounds on the fibers shows better electric conductivity in spite of the fact that oxidized substances of metals are poorer in electric conductivity than metals or alloys, is caused in part by a continuation of metal powder on the surface of fibers. It is also assumed that the metal on the fiber surfaces is electrically charged because of its oxidized state, and as a result, molecules such as water and carbon dioxide having polarity are coordinated secondarily with the metal particles therebetween to promote the flow of current.

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TABLE 2
electric resistivity (Ω/cm)

Temperature of the surface of yarns	Amount of brass attached (g/m)	Tenacity	Elongation	before sulfurizing	after sulfurizing
Untreated yarns	0	3.7 g/d	28%	$10^{12} \Omega/\text{cm}$ or more	$10^{12} \Omega/\text{cm}$ or more
Yarns heat-treated at 130°C	10^{-13} or less	3.8 ,	25%	10^{12} or more	10^{12} or more
Yarns heat-treated at 190°C	5.6×10^{-6}	3.1 ,	24%	3×10^{10}	3×10^2
Yarns heat-treated at 220°C	6.3×10^{-5}	1.2 ,	13%	5×10^{10}	8×10^2

Comparative Example 1.

Dried nylon 6 chips (relative viscosity as measured in 98% sulfuric acid at 25°C : 2.42, m.p.: 218°C) were subjected to melt-spinning, followed by stretching to give monofilaments of 150d having a tenacity of 3.88 g/d and an elongation of 25%.

5 The above-mentioned fibers were subjected to an adhesion test of brass powder having a mean particle diameter of 2μ (composition of copper/zinc of 70/30 by weight) in a similar manner to that of Example 1. As a result, when the temperature in a heating cylinder was below 210°C , almost no adhesion of the powder onto the fiber surface occurred, while, when the heat-treating temperatures were elevated above 210°C and the resulting fibers were taken up, fiber breakage very often occurred and continuous take-up became difficult. The tenacity of fibers subjected to adhesion by heating at a surface temperature of 220°C as measured was 2.16 g/d, that is, the reduction in tenacity was remarkable.

10 25 However, the metal powder-carrying fibers obtained by making brass powder adhere by heating at 220°C had an amount of brass powder made to adhere, of 4.3×10^{-5} g/m, and after the sulfurizing treatment, superior 30 conductive fibers having an electric resistivity of $3 \times 10^2 \Omega/\text{cm}$ were obtained.

Example 2.

35 Composite filament yarns of concentric sheath and core type having a sheath/core ratio of 1:1 consisting of various kinds of thermoplastic high molecular weight polymers as shown in Table 3 were prepared using a conventional sheath and core type composite spinning machine, followed by stretching

according to a conventional method to give stretched composite yarns of 70 d/gf. As in Example 1, brass powder having a copper/zinc ratio of 70/30 by weight and a mean particle diameter of 2μ was allowed to adhere by heating onto the surface of the resulting yarns using the apparatus of Fig. 1, and the heat-adhesiveness of the powder to the composite yarns were observed by a microscope. The temperature of the surface of the filament yarns was about 20°C lower than the respective melting points of the thermoplastic high molecular weight polymers of the core at the time of treatment in the heating cylinder.

40 45 50 55 As for the adhesiveness of the metal powder onto the high molecular weight polymers, fastness to rubbing by washing was examined. The results are shown in Table 3. When the sheath of composite filament yarns was of polyethylene, polypropylene or polyesters, peeling-off of the metal powder by rubbing by washing due to the weak adhesiveness of the powder onto the polymers was observed.

60 65 On the other hand, in case of polyamide, no peeling-off of the powder by rubbing during the time of washing occurred due to the superior adhesiveness of the powder into polyamides.

70 Accordingly, in order to obtain conductive yarns having a superior durability, it is preferable to utilize a high molecular weight polymer of polyamide group having a superior adhesiveness of metal powders thereto.

75 After washing with a solution of a detergent three times and with water five times, each 50 g of metal powder-carrying fibers was subjected to sulfurizing treatment as in Example 1 and their electric resistivities were measured. The results are shown in Table 3.

TABLE 3

High molecular weight polymer of sheath component	High molecular weight polymer of core component	Surface temperature of fibers	Amount of brass powder attached (g/m)			Electric resistivity after sulfurizing treatment (Ω/cm)
			before washing	1st wash	2nd wash	
Polyethylene	Nylon 6	190°C	2.2x10 ⁻³	4x10 ⁻⁴	1.5x10 ⁻⁴	6.7x10 ⁻²
(1) MI=2.2 Mp=137°C	(5) $\eta_r=2.42$ Mp=218°C					8.6×10^4
Polypropylene	Nylon 66	227°C	2.4x10 ⁻³	1.3x10 ⁻³	3.4x10 ⁻⁴	1.7x10 ⁻³
(1) MI=3.6 Mp=176°C	(5) $\eta_r=2.42$ Mp=25.7°C					3.5×10^4
Copolyester (3)	Polyethylene-terephthalate	235°C	6.4x10 ⁻⁵	7.8x10 ⁻⁵	5.3x10 ⁻⁵	8.4x10 ⁻⁵
(2) [η]=0.63 Mp=202°C	(2) [η]=0.82 Mp=259°C					2.2×10^4
Copolyamide (4)	Nylon 6	190°C	7.8x10 ⁻³	6.3x10 ⁻³	6.1x10 ⁻³	5.4×10^3
(5) $\eta_r=2.52$ Mp=140°C	(5) $\eta_r=2.42$ Mp=218°C					1.3×10^3

(1) MI means a melt index at 200°C.

(2) [η] is an intrinsic viscosity as measured in orthochlorophenol solution at 35°C.

(3) Copolyester of terephthalic acid, adipic acid and ethylene glycol.

(4) Copolyamide of nylon 6 and nylon 6, 12.

(5) η_r is relative viscosity measured—98% sulfuric acid at 25°C.

Example 3.

Copper powder (mean particle diameter of 1.5μ), zinc powder (mean particle diameter of 1.5μ), brass powder (mean particle diameter of 2μ), aluminum powder (mean particle diameter of 2μ), iron powder (mean particle diameter of 3μ), silver powder (mean particle diameter of 1.5μ) and lead powder (mean particle diameter of 3μ) were respectively made to adhere by heating at 210°C , using the processing steps described with respect to Fig. 1, onto the surface of composite filament yarns consisting of polyethylene terephthalate (intrinsic viscosity $[\eta]$ as measured in *o*-chlorophenol at 35°C : 0.82, m.p.: 259°C) as a core component and three component-copolyamide of nylon 6/nylon 66/nylon 612 (relative viscosity η_r as measured in 98% sulfuric acid at 25°C : 2.48, m.p.: 153°C , composition: 50/20/30 by mol) as a sheath component. The fiber surface of the resulting metal powder-carrying yarns, were uniformly coated by metal powder, each showing characteristic luster of metal powder, and even after three times washing with a 5% aqueous solution of a neutral detergent and five times washing with water, no peeling-off of metal powder was observed. The amount of adhesion was 10^{-5} — 10^{-3} g/m.

The electric resistivities after washing, of the metal powder-carrying yarns, were measured using an electric resistance-measuring instrument of TR-6S type (manufactured by Takeda Riken K.K., Japan) under the atmosphere of relative humidity of 40% and temperature of 25°C . As a result, as shown in Column 4 of Table 4, the electric resistivities of the metal powder-carrying yarns were unexpectedly high, that is, as high as $10^{10} \Omega/\text{cm}$, in spite of the good electric conductivities of the metals themselves, as shown in Column 2 of Table 4. Thus, a product to be called conductive yarns could not be obtained.

The respective metal powder-carrying yarns as above-mentioned were reeled each in an amount of 100 g, and the resulting skeins were allowed to stand at room temperature in a desiccator at relative humidity of 100% in an atmosphere having a partial pressure of hydrogen sulfide of 500 mm Hg. The metal powder on the fiber surface was at once subjected to sulfurizing whereby the color changed to black characteristic of metal sulfides. Conversion of the metal powder into sulfide was about 90~95%.

After two hours of the sulfurizing treatment of the metal powder on the fiber surface, the skeins were taken out and water-washed. Almost no peeling-off of metal sulfides occurred.

Then, drying was carried out at 105°C for 6 hours, and the electric resistances of the yarns coated by metal sulfide were measured as in Example 1.

The results are shown in Column 5 of Table 4.

In spite of the fact that the conductivities of simple substances of metals are lessened by oxidation, the yarns coated by metal sulfide had, to be surprising enough, a hundred thousand times or more the conductivities of the yarns coated by the metal powder.

Example 4.

The composite yarns of concentric sheath and core type consisting of a heat-melt-adhesive polyamide of a low melting point (m.p. 153°C) as a sheath component and polyethylene terephthalate (m.p. 259°C) as a core component (having a sheath/core volume ratio of 2:1), obtained in Example 3, were subjected to adhesion of copper powder thereto using the apparatus of Fig. 1, and successively the copper powder (mean particle diameter of 1.5μ) on the fiber surface was subjected to sulfurizing treatment with hydrogen sulfide gas.

Namely, composite yarns 2 were allowed to run through the inside of a powder container 5 provided with a vibration apparatus 10 and containing copper powder 4 (mean particle diameter of 1.5μ) at a velocity of 50 m/min., and then led to a heat-treatment cylinder 6 having an inner diameter of 70 mm and a length of 1500 mm, wherein copper powder was made to adhere by heating onto the fiber surface having a temperature of 230°C . Successively, the copper powder-carrying yarns were led into a chamber containing hydrogen sulfide gas, at an inner temperature of 60°C and a relative humidity of 100%, and wound up on a reel made from nylon and having a radius of 400 mm, in the atmosphere of hydrogen sulfide gas. After reeling up about 500 g, the yarns were retained in the atmosphere of hydrogen sulfide gas further for 10 minutes.

After complete purging of hydrogen sulfide gas, the resulting skein was taken out. It was found that the fiber surface was completely coated with black copper sulfide. The adhesion amount was 2.7×10^{-4} g based on copper. The yarns coated with copper sulfide were dried, and their electric resistivity was measured. It was $9 \times 10^2 \Omega/\text{cm}$. Namely, the resulting yarns had a superior conductivity.

Example 5.

100 g of each of the metal powder-carrying yarns obtained in Example 3, were wound up on reels and allowed to stand for seven days in an atmosphere having a partial pressure of oxygen gas of 400 mm Hg at a relative humidity of 100%, and a temperature of 80°C , until the metal powder on the fiber surface completely turned into the characteristic color of oxide of the metal. After the oxidation treatment, the resulting yarns coated with metal oxides were dried at 105°C for 6 hours; and

their electric resistances were measured. The results are shown in Table 4. As seen in Column 7 of Table 4, conductive yarns having a remarkably reduced electric resistance were obtained.

Example 6.

100 g of each of the composite yarns onto which powder of copper, zinc or silver were allowed to adhere, obtained in Example 3, were wound up on reels and the metal powder on the fiber surface was subjected to chlorination treatment in an atmosphere having a relative humidity of 100% and a partial pressure of chlorine gas of 100 mm Hg. After the chlorination treatment, the resulting skeins

were taken out and washed with water. As a result, water-soluble copper chloride (green) and zinc chloride (colorless) absorbed a large amount of water and when washed with water, they are washed away, and the yarns returned to the original mere composite yarns.

On the other hand, in the case of silver chloride (yellowish white color) which is hardly soluble, it was not washed away by water-washing carried out one time.

As seen from this example, hardly soluble or insoluble metal compounds are preferable as the metal compounds (oxidized products of metals) from the viewpoint of fastness to washing.

TABLE 4

Kind of metals	Copper	Zinc	Brass	Aluminum	Iron	Silver	Lead
Electric resistivity of simple substance of metal	$1.72 \times 10^{-6} \Omega/\text{cm}$	$6 \times 10^{-6} \Omega/\text{cm}$	$5-7 \times 10^{-6} \Omega/\text{cm}$	$2.75 \times 10^{-6} \Omega/\text{cm}$	$9.8 \times 10^{-6} \Omega/\text{cm}$	$1.62 \times 10^{-6} \Omega/\text{cm}$	$2.1 \times 10^{-6} \Omega/\text{cm}$
Adhesion amount of metal powder	$1.8 \times 10^{-4} \text{ g/m}^2$	$1.6 \times 10^{-4} \text{ g/m}^2$	$2.0 \times 10^{-4} \text{ g/m}^2$	$5.4 \times 10^{-5} \text{ g/m}^2$	$1.03 \times 10^{-5} \text{ g/m}^2$	$2.5 \times 10^{-5} \text{ g/m}^2$	$2.3 \times 10^{-5} \text{ g/m}^2$
Yarns coated with metals	Ex. 3	$3-4 \times 10^{-10} \Omega/\text{cm}$	$8 \times 10^{-11} \Omega/\text{cm}$	$1 \times 10^{-11} \Omega/\text{cm}$	$2 \times 10^{-11} \Omega/\text{cm}$	$8 \times 10^{-11} \Omega/\text{cm}$	$8-9 \times 10^{-9} \Omega/\text{cm}$
Electric resistivity of yarns coated with metal sulfide	Ex. 3	$7 \times 10^{-2} \Omega/\text{cm}$	$1 \times 10^{-1} \Omega/\text{cm}$	$9 \times 10^{-2} \Omega/\text{cm}$	$6 \times 10^{-1} \Omega/\text{cm}$	$5-6 \times 10^{-1} \Omega/\text{cm}$	$8 \times 10^{-1} \Omega/\text{cm}$
Electric resistivity of yarns coated with metal oxide	Ex. 5	$2 \times 10^{-1} \Omega/\text{cm}$	$6 \times 10^{-1} \Omega/\text{cm}$	$3 \times 10^{-1} \Omega/\text{cm}$	$7 \times 10^{-1} \Omega/\text{cm}$	$8 \times 10^{-1} \Omega/\text{cm}$	$6 \times 10^{-1} \Omega/\text{cm}$
Electric resistivity of yarns coated with metal chloride	Ex. 6	Washed away	Washed away			$8 \times 10^{-1} \Omega/\text{cm}$	
Electric resistivity of yarns coated with metal carbonate		$7 \times 10^{-3} \Omega/\text{cm}$	$2 \times 10^{-4} \Omega/\text{cm}$	$9 \times 10^{-3} \Omega/\text{cm}$	$1 \times 10^{-3} \Omega/\text{cm}$	$3 \times 10^{-1} \Omega/\text{cm}$	

Example 7.

Composite yarns coated with copper sulfide, obtained in Example 4, were arranged together with raw yarns of nylon 66 of 840d/48f for carpet manufacture and tufted into a carpet. As for conditions of arrangement, one of the yarns coated with copper sulfide per 10 yarns of nylon 66 was tufted. Further, for comparison, commercially available conductive yarns (electric resistivity: 10 Ω/cm) silver-plated according to a chemical plating method were similarly mixed and tufted into a carpet.

The electric charge of the carpets thus prepared was measured at a relative humidity of 30%, according to the measurement method of 15 "The body voltage build-up for the carpet" proposed by "American Carpet Institute Subcommittee". The results are shown in Table 5. As apparent from this Table, the conductive yarns according to the present invention have 20 a conductivity comparable to those according to a chemical plating method.

TABLE 5

Sample	Charged voltage in human body
Carpet of nylon 66 yarns	5000 V
Carpet of nylon 66 yarns arranged with those coated with copper sulfide	200 V
Carpet of nylon 66 yarns arranged with silver-plated conductive yarns	160 V
Carpet of wool	1800 V

Note: According to the above-mentioned measurement method, carpets having a charged voltage in human body, of 1000 V or lower are deemed preferable.

WHAT WE CLAIM IS:—

25 1. A conductive synthetic fiber having an electric resistivity of 10^3 ohm/cm or less comprising a layer of a metal compound on the surface of a thermoplastic synthetic polymer fiber, said metal compound being obtained by treatment as hercin defined in an oxidising atmosphere.

30 2. A fiber according to claim 1 wherein the subjecting metal powder attached to the surface of said thermoplastic synthetic polymer fiber to an oxidation treatment as herein defined, the metal compound being insoluble in water and dry cleaning solvents.

35 3. A fiber according to claim 1 or 2, wherein at least the surface portion of the thermoplastic synthetic polymer fiber consists of a polyamide.

40 4. A fiber according to any one of claims 1 to 3, wherein the metal compound is a metal sulfide or metal oxide.

45 5. A conductive fiber according to claim 1 substantially as described in any one of the Examples.

50 6. A method for producing conductive fibers which comprises attaching metal powder to the surface of thermoplastic synthetic polymer fibers to cover substantially the whole surface of the fibers, and subjecting the resulting metal-powder-carrying fibers to an oxidation treatment according to claim 7 proposed by "American Carpet Institute Subcommittee". The results are shown in Table 5. As apparent from this Table, the conductive yarns according to the present invention have a conductivity comparable to those according to a chemical plating method.

55 7. A method according to claim 6 wherein at least the surface portion of the thermoplastic synthetic polymer fibers consists of a polyamide.

60 8. A method according to claim 7, wherein the thermoplastic synthetic polymer fibers have sheath and core type construction and the sheath part consists of a polyamide having a melting point lower than that of the core part component.

65 9. A method according to any one of claims 6 to 8, wherein the metal of the metal powder is copper, zinc, lead, silver, aluminium, iron or an alloy of the foregoing metals.

70 10. A method according to any one of claims 6 to 9, wherein the oxidation treatment is sulfurization.

75 11. A method for producing conductive fibers according to any one of claims 6 to 9, wherein the oxidation treatment is heating in an oxygen containing gas.

80 12. A method according to any one of claims 6 to 11, wherein the attachment of metal powder to the surface of the thermoplastic synthetic polymer is carried out after treating the fibers with water.

13. A method according to claim 6 substantially as described in any one of the Examples.

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Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1975.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.

1396072

COMPLETE SPECIFICATION

2 SHEETS

*This drawing is a reproduction of
the Original on a reduced scale
Sheet 1*

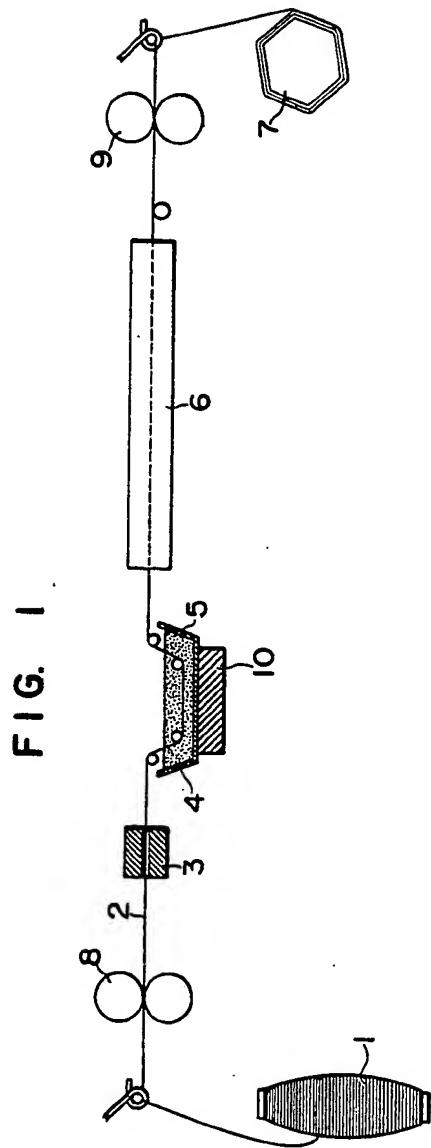


FIG. 2

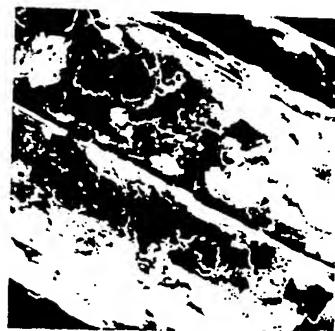


FIG. 3

